Unit 6

Answers: Periodic Table

Quick checks

1 c The modern table is ordered by atomic number, the number of protons. Argon's extra neutrons make it heavier, but it has one proton fewer, so it comes first. (Argon has 22 neutrons in its common isotope, potassium 20: more, not fewer.)

2 c Its last electron, by the Aufbau order, goes into 3d, so it is in the d block; 5 d electrons + 2 s electrons = group 7. It is manganese. The $4s^2$ doesn't make it an s-block element: every element after calcium in period 4 has 4s electrons.

3 b Both kinds are metals that form positive ions, conduct and react with chlorine. Only the transition metals have partly filled d subshells, which give colored compounds and let them lose different numbers of electrons.

4 b Chlorine is more reactive than iodine, so it displaces it: $Cl_2 + 2KI \rightarrow 2KCl + I_2$. The iodine colors the solution brown. Potassium chloride is soluble, so no precipitate forms.

1 a. **c** Hund's rule. Aufbau gives the order of the subshells, and Pauli the limit of two electrons, of opposite spin, in an orbital.

1 b. **b** A half-filled 3d subshell is extra stable, so one electron moves from 4s to 3d: [Ar] $4s^1\ 3d^5$.

1 c. **d** Size increases down a group and decreases across a period. Potassium is lowest in group 1, with four shells: 203 pm.

1 d. **b** Chlorine, 349 kJ/mol. Fluorine (328) is so small that its crowded 2p electrons repel an incoming electron. Neon forms no stable negative ion.

1 e. **c** The ns and (n − 1)d subshells are close in energy, so an atom can lose its ns electrons alone or some d electrons as well: iron forms Fe^{2+} and Fe^{3+}.

2 a. An element's properties depend on its outer electronic configuration. As the atomic number increases, the same outer configurations come back after each noble gas: ns^1 after every noble gas, $ns^2\ np^5$ just before every noble gas. Elements with the same outer configuration fall in one group and have similar properties, so properties repeat periodically.

2 b. Electrons fill the subshell of lowest energy first (Aufbau). For 4s, $n + l = 4 + 0 = 4$; for 3d, $3 + 2 = 5$. 4s has the lower energy, so after argon's 18 electrons fill up to 3p, the 19th electron goes into 4s.

2 c. At copper, 4s and 3d are very close in energy. A completely filled d subshell (d^{10}) is especially stable, so the atom has a lower energy when one 4s electron moves into 3d to fill it. Hence [Ar] $4s^1\ 3d^{10}$.

2 d. All the elements from sodium to chlorine have three shells, but each step adds one proton to the nucleus while the new electron goes into the same outer shell, which shields it very little. The pull felt by the outer electrons rises (roughly +1 for sodium to +7 for chlorine), drawing the shell closer, so the radius falls from 166 pm to 102 pm.

2 e. Magnesium is [Ne] $3s^2$, a filled s subshell. Aluminium is [Ne] $3s^2\ 3p^1$: its outermost electron is in 3p, which is higher in energy than 3s and shielded by the 3s electrons, so it is removed more easily (578 kJ/mol) than one of magnesium's 3s electrons (738 kJ/mol).

2 f. Fluorine is very small, so its outer 2p subshell is crowded: an incoming electron is strongly repelled by the seven electrons already there. Chlorine's 3p subshell is larger, and the repulsion is less, so more energy is released when chlorine gains an electron (349 kJ/mol) than when fluorine does (328 kJ/mol).

2 g. Nitrogen is quite electronegative (3.04), but its atoms are joined in N_2 by a triple bond, one of the strongest bonds known (about 945 kJ/mol). This bond must be broken before nitrogen can react, so it reacts only at high temperatures, as in lightning or the Haber process.

2 h. Color in transition metal compounds comes from d electrons jumping between d orbitals of slightly different energy, absorbing part of visible light. Cu^{2+} is [Ar] $3d^9$, with a partly filled d subshell, so its compounds absorb light and look colored (copper sulphate is blue). Zn^{2+} is [Ar] $3d^{10}$: its d subshell is full, no such jumps are possible, and its compounds are white.

3 i.

s-block elements	p-block elements
Groups 1 and 2 (and helium).	Groups 13 to 18.
Last electron enters an s subshell: ns^1 or ns^2.	Last electron enters a p subshell: $ns^2\ np^1$ to $ns^2\ np^6$.
All metals, except hydrogen and helium.	Metals, metalloids, non-metals and noble gases.
Low ionization potentials: they lose electrons, forming positive ions.	Mostly high ionization potentials and electron affinities: they gain or share electrons.
Fixed valency (1 or 2).	Often variable valency (P 3 and 5; S 2, 4, 6).
Their oxides are basic.	Their non-metals' oxides are acidic.

3 ii.

d-block elements	f-block elements
Last electron enters the (n − 1)d subshell.	Last electron enters the (n − 2)f subshell.
Groups 3 to 12, in the middle of the table.	The two rows printed below the table.
Four series: 3d, 4d, 5d and 6d.	Two series, lanthanides (4f) and actinides (5f), 15 elements each.
Called transition elements.	Called inner transition elements.
Properties change noticeably along a series; variable valency is common.	Properties within a series are very similar; valency 3 is most common.
Only technetium and the elements after 103 are radioactive.	All the actinides are radioactive.

3 iii.

Ionization potential	Electron affinity
Energy needed to **remove** the most loosely held electron from an isolated gaseous atom.	Energy **released** when an electron is **added** to an isolated gaseous atom.
$X(g) \rightarrow X^{+}(g) + e^{-}$; forms a positive ion.	$X(g) + e^{-} \rightarrow X^{-}(g)$; forms a negative ion.
Energy is always taken in.	Energy is usually released.
Highest for the noble gases, lowest for the alkali metals.	Highest for the halogens; the noble gases form no stable negative ion.

3 iv.

Electron affinity	Electronegativity
A property of an isolated atom.	A property of an atom in a molecule (in a bond).
The energy released when the atom gains an electron.	The tendency of the atom to attract a shared pair of electrons.
An energy, measured in kJ/mol or eV.	A number on a scale (Pauling's), with no unit.
Highest for chlorine.	Highest for fluorine.

4 a. **Modern periodic law:** the physical and chemical properties of the elements are periodic functions of their atomic numbers.
Merits (any three):

- It is based on atomic number, a basic property of the atom.
- The positions of Ar and K, Co and Ni, and Te and I, out of order by atomic mass, are correct by atomic number.
- Isotopes have the same atomic number, so they need only one place.
- It explains why properties repeat: the outer configuration repeats.
- Metals, non-metals and metalloids are in separate regions, and the transition metals have a block of their own.

4 b. A period begins with a new shell's s subshell and ends when that shell's p subshell is full, and its length is the number of electrons the subshells it fills can hold. Period 1 fills only 1s: 2. Periods 2 and 3 fill ns and np: $2 + 6 = 8$ (3d is too high in energy to fill in period 3). Periods 4 and 5 fill ns, $(n - 1)$d and np: $2 + 10 + 6 = 18$. (Periods 6 and 7 also fill an f subshell: $2 + 14 + 10 + 6 = 32$.)

4 c.

- **Aufbau principle:** electrons fill the subshells in order of increasing energy, 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p…
- **Pauli's exclusion principle:** an orbital holds at most two electrons, and they must have opposite spins.
- **Hund's rule:** electrons go into the orbitals of a subshell singly, with parallel spins, before any pair up.

Oxygen (8): $1s^2\ 2s^2\ 2p^4$.
1s: ↑↓ 2s: ↑↓ 2p: ↑↓ · ↑ · ↑
It has 2 unpaired electrons.

4 d.

Z	Configuration	Block	Period	Group
11 (Na)	$1s^2\ 2s^2\ 2p^6\ 3s^1 = [Ne]\ 3s^1$	s	3	1
16 (S)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4 = [Ne]\ 3s^2\ 3p^4$	p	3	$12 + 4 = 16$
21 (Sc)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1 = [Ar]\ 4s^2\ 3d^1$	d	4	$1 + 2 = 3$
29 (Cu)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10} = [Ar]\ 4s^1\ 3d^{10}$	d	4	$10 + 1 = 11$

4 e. **s-block (any four):** soft, light metals with low melting points (except H and He); low ionization potentials, forming M^+ or M^{2+}; fixed valency 1 or 2; very reactive, so never found free; mostly ionic compounds with basic oxides; many color flames; compounds usually colorless.

d-block (any four): hard metals with high melting and boiling points; variable valency (Fe 2, 3; Cu 1, 2); colored compounds; many are catalysts (Fe, Ni, V_2O_5, Pt); many are paramagnetic; form alloys and complex ions; atomic sizes nearly the same along a series.

4 f. **Ionization potential** is the minimum energy needed to remove the most loosely held electron from an isolated gaseous atom: $X(g) \rightarrow X^+(g) + e^-$. It is measured in eV per atom or kJ/mol.

In a period it generally **increases** from left to right: the nuclear charge increases while the electrons enter the same shell, so the atoms get smaller and hold their outer electrons more tightly (Na 496 → Ar 1,521 kJ/mol). Small dips occur where a new subshell starts (Mg > Al) or an electron must pair up (P > S).

In a group it **decreases** from top to bottom: each step adds a new shell, so the outer electron is farther from the nucleus and better shielded by inner electrons (Li 520 → Cs 376 kJ/mol).

4 g. **Electronegativity** is the tendency of an atom in a molecule to attract the shared pair of electrons of a covalent bond towards itself. It is measured on Pauling's scale, which has no unit.

It **increases across a period** (atoms smaller, more nuclear charge felt) and **decreases down a group** (atoms larger, outer electrons farther and better shielded). The most electronegative element is **fluorine** (3.98), at the top right; the least are **cesium** (0.79) and francium, at the bottom left.

4 h. The reactivity of alkali metals **increases down the group**: Li < Na < K < Rb < Cs. All react by losing their single outer (ns^1) electron. Down the group the atoms get larger, the outer electron is farther out and better shielded, and the ionization potential falls (520, 496, 419, 403, 376 kJ/mol), so the electron is lost more easily. Potassium reacts with cold water so fast that the hydrogen catches fire with a lilac flame:

$$2 + 2_2 \rightarrow 2 + {}_2$$

Lithium only fizzes steadily, while rubidium and cesium explode.

4 i. The reactivity of halogens **decreases down the group**: F > Cl > Br > I. They react by gaining an electron, and down the group the atoms are larger, so the incoming electron is attracted less strongly (electronegativity falls from 3.98 to 2.66).
Experiment (displacement): add chlorine water to potassium bromide and potassium iodide solutions in two test tubes. The first turns orange-yellow (bromine set free), the second brown (iodine set free):

$$_2 + 2 \rightarrow 2 + _2 \qquad _2 + 2 \rightarrow 2 + _2$$

Bromine water added to potassium iodide also sets iodine free, $_2 + 2 \rightarrow 2 + _2$, but iodine added to potassium chloride or bromide does nothing. So Cl > Br > I.

4 j. All have the outer configuration $ns^2\,np^3$ and valency 3 (and 5 from phosphorus on).
Metallic character increases down the group: nitrogen and phosphorus are non-metals, arsenic and antimony metalloids, bismuth a metal; their oxides change from acidic (N_2O_5, P_4O_{10}) to basic (Bi_2O_3).
In reactivity, **nitrogen** is very unreactive because of the strong triple bond in N_2, reacting only at high temperature (lightning, the Haber process). **White phosphorus** is very reactive, catching fire in air at about 30 °C, because its strained P_4 molecules break apart easily. Below them, the tendency to gain electrons falls steadily as the atoms grow.

5 a. A (9) [He] $2s^2\,2p^5$: group 17, period 2 (fluorine). B (12) [Ne] $3s^2$: group 2, period 3 (magnesium). C (17) [Ne] $3s^2\,3p^5$: group 17, period 3 (chlorine). D (20) [Ar] $4s^2$: group 2, period 4 (calcium).

i. **A and C** are both in group 17 (and B and D both in group 2).

ii. **A**: it is higher in group 17, smaller, and more electronegative.

iii. **D**: it is lower in group 2, so it loses its two outer electrons more easily than B.

iv. B has valency 2 and C valency 1: **BC_2** ($MgCl_2$).

5 b. i. The first three energies rise steadily; the fourth jumps more than four times, because the fourth electron must come out of a full inner shell. So Y has **3 valence electrons**.

ii. **Group 13** (it is aluminium, [Ne] $3s^2\,3p^1$).

iii. Valency 3 against oxygen's 2: **Y_2O_3**.

5 c. Moles of Cl atoms $= \frac{3.55}{35.5} = 0.1$ mol.
Energy released $= 0.1 \times 349 =$ **34.9 kJ**.

5 d.

i. P: [Ne] $3s^2\ 3p^3$, three 3p electrons one to an orbital: **3**.

ii. Fe: [Ar] $4s^2\ 3d^6$, 3d is ↑↓ ↑ ↑ ↑ ↑: **4**.

iii. Fe^{3+}: [Ar] $3d^5$, one in each 3d orbital: **5**.

iv. Cr: [Ar] $4s^1\ 3d^5$, five in 3d and one in 4s: **6**.

The more unpaired electrons, the more strongly paramagnetic a substance is, so of these, **chromium atoms** (6) would be pulled most strongly, then Fe^{3+}. (Iron metal itself is far more magnetic than any of these, because it is ferromagnetic: its atoms' magnets line up together in domains.)

5 e.

i. **Na > Mg > Al > Cl** (166, 141, 121, 102 pm): same shells, more protons pulling.

ii. **F > Cl > Br > I** (3.98, 3.16, 2.96, 2.66): down the group the atoms grow and pull shared electrons less.

iii. **Li > Na > K** (520, 496, 419 kJ/mol): down the group the outer electron is farther and better shielded.

iv. **Mg^{2+} < Na^+ < Na < Cl^-** (72, 102, 166, 181 pm). Mg^{2+} and Na^+ both have 10 electrons, but Mg^{2+} has 12 protons pulling them to Na^+'s 11; the sodium atom still has its third shell; Cl^- has a third shell holding 8 electrons.

5 f. More particles don't make an atom bigger; the size of an atom is set by how far out its outer shell is. Lithium and fluorine both have two shells (K and L), so their outer electrons are in the same shell. Fluorine's 9 protons pull its L shell, which feels about +7 after the two inner electrons shield it, much more strongly than lithium's 3 protons pull its single L electron, which feels about +1. So the fluorine atom is far **smaller**: its covalent radius is 57 pm, against lithium's 128 pm. Its nucleus is heavier, but the nucleus is tiny; the electrons decide the size.